

# High frequency acoustic modes in liquid gallium at the melting point.

T. Scopigno<sup>1</sup>, A. Filippini<sup>2</sup>, M. Krisch<sup>3</sup> G. Monaco<sup>3</sup> G. Ruocco<sup>1</sup>, F. Sette<sup>3</sup>

<sup>1</sup>*Dipartimento di Fisica and INFN,*

*Universitá di Roma “La Sapienza”, I-00185, Roma, Italy.*

<sup>2</sup>*Dipartimento di Fisica and INFN,*

*Universitá di L’Aquila, I-67010, L’Aquila, Italy.*

<sup>3</sup>*European Synchrotron Radiation Facility,*

*B.P. 220 F-38043 Grenoble, Cedex France.*

(Dated: August 14, 2002)

## Abstract

The microscopic dynamics in liquid gallium (l-Ga) at melting ( $T=315$  K) has been studied by inelastic x-ray scattering. We demonstrate the existence of collective acoustic-like modes up to wave-vectors above one half of the first maximum of the static structure factor, at variance with earlier results from inelastic neutron scattering data [F.J. Bermejo et al. Phys. Rev. E **49**, 3133 (1994)]. Despite the structural (an extremely rich polymorphism and rather complex phase diagram) and electronic (mixed valence) peculiarity of l-Ga, its collective dynamics is strikingly similar to the one of Van der Walls and alkali metals liquids. This result speaks in favor of the universality of the short time dynamics in monatomic liquids rather than of system-specific dynamics.

PACS numbers: 67.55.Jd; 67.40.Fd; 61.10.Eq; 63.50.+x

The nature of the microscopic dynamics in simple fluids is nowadays one of the most lively debated topics in the condensed matter field. The provocative evidence of well defined collective excitations outside the truly hydrodynamic region has attracted many experimentalists in the last three decades. In particular, several studies performed through Inelastic Neutron Scattering (INS) revealed the presence of a Brillouin triplet in the dynamic structure factor of many monatomic liquids [1]. Together with numerical studies [2] these experiments provided us some pictures of the high frequency dynamics, although a deep comprehension of the ultimate nature of these excitations is still missing [3, 4]. More recently, the advent of the new radiation sources has allowed the full development of the Inelastic X-ray Scattering (IXS) [5]. This technique, being sensitive to the coherent dynamics only and allowing to investigate the low exchanged momentum ( $Q$ ) region inaccessible to INS, renewed the interest and the efforts in the field giving rise to a number of experiments [6]. More specifically, some light has been shed on the mesoscopic dynamics of different monatomic systems as Van der Walls fluids (He, Ne), liquid alkali metals (Li, Na), and more complex liquid metals (Al). In particular, using the generalized Langevin equation formalism, the presence of two viscous relaxation processes has been experimentally proven in all these systems, and the relevant parameters have been quantitatively determined [7].

Among the elemental liquid metals, Ga exhibits peculiar structural and electronic properties. In addition to the low melting point ( $T_m = 303$  K), it presents an extended solid phase polymorphism with complex crystal structures where a competition between metallic and covalent bonding character takes place [8]. Although the electronic DOS in l-Ga is nearly free electron it still shows anomalies associated with some covalency residue. Moreover, the first peak of the  $S(q)$  presents a hump characteristics of non close-packed liquid structures [9]. The existence of common features in the high frequency dynamics of all the monatomic liquids seems to be challenged by liquid Gallium. In fact, earlier studies performed by INS showed somehow contradictory results. At room temperature, although no collective modes were visible in the experimental data, the spectra were described by a damped harmonic oscillator model, and the excitation frequencies were found to lie above the hydrodynamic values. This effect was ascribed to the presence of high frequency optical modes that were supposed to contribute to the spectra. In these studies, the absence of acoustic excitations was explained with a high value of the longitudinal viscosity, despite on the basis of hydrodynamic arguments collective modes should have been expected [10]. Few years later, a

new INS experiment was performed at higher temperature ( $T=973$  K), and collective modes were detected. In particular, at low wavevectors an acoustic mode was found, while at high wave-vectors the dispersion curve split in two branches that according to the authors should be associated to acoustic and optic excitations respectively [11]. This picture (absence of acoustic-like excitations just above melting) -if verified- would stress the anomalous dynamical behaviour of Gallium, and would falsify the idea of a common high frequency dynamics of monatomic systems.

In this paper we report on an inelastic x-ray scattering study of the microscopic dynamics in liquid gallium just above the melting point. The sensitivity of this technique to the purely collective motion only and the extended accessible cinematic region, allowed an accurate determination of the coherent dynamic structure factor. We find clear indication of acoustic-like excitations, whose properties parallel those of all the other investigated monatomic liquids. Moreover, the value of the transport coefficients derived by a generalized Langevin equation description of the spectra, quantitatively agrees with the hydrodynamic expectations. The obtained results indicate that -despite its structural and electronic anomalies- liquid Gallium shares with the other simple liquids (metals and non-metals) the same features of the high frequency atomic dynamics.

The experiment has been performed at the ID28 beam-line of the ESRF at fixed exchanged wave-vector over a  $Q-$  region below the position of the main diffraction peak ( $Q_M \approx 25 \text{ nm}^{-1}$ ). A typical energy scan ( $-50 < E < 50 \text{ meV}$ ) took about 300 minutes, and was repeated for a total integration time of about 300 seconds/point. A five analyzers bench allowed us to collect simultaneously spectra at five different values of the exchanged wave-vector  $Q$  for each single scan. The sample consisted of a gallium molten droplet kept in sandwich between two sapphire windows (thickness 0.25 mm). The sample thickness, ( $\approx 100\mu\text{m}$ ), was chosen in order to match the absorption length at the incident energy of 17794 eV, corresponding to the (9 9 9) reflection from the silicon analyzers that we utilized ( $\delta E \approx 3.0 \text{ meV}$ ) [5].

In Fig. 1 we report the measured IXS intensity for each investigated (fixed)  $Q$ -value. The presence of an acoustic propagating mode clearly appears from the raw data. These modes were not observed in Ref. [10], probably due to the limited accessible cinematic region and to the incoherent scattering contribution to the spectra. The spurious signal coming from the longitudinal and transverse phonons of the sapphire windows, due to the high value

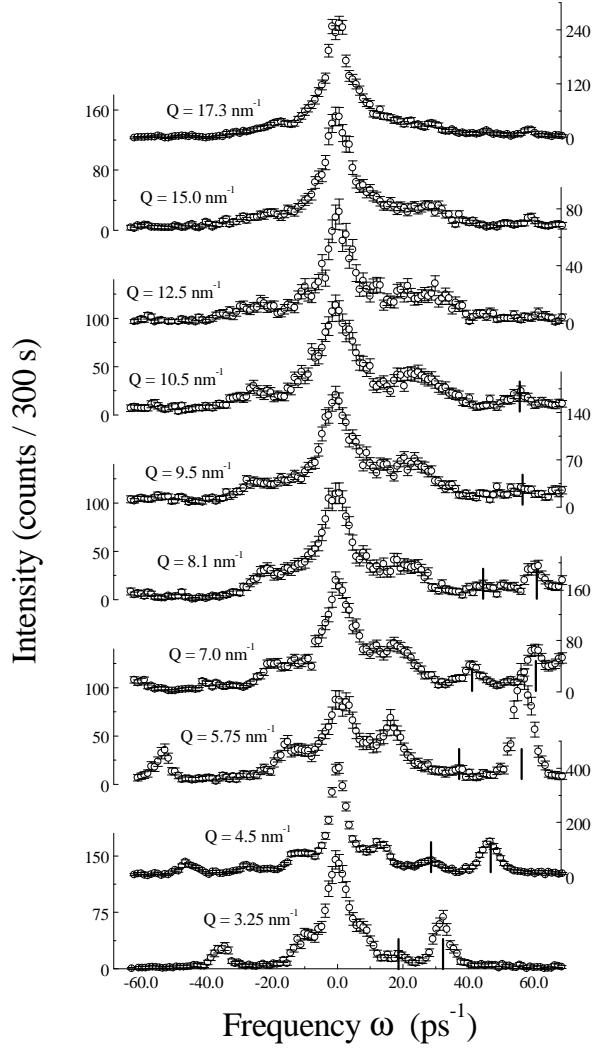


FIG. 1: IXS spectra of liquid Ga ( $T = 315$  K) at the indicated  $Q$  values. The vertical bars indicate the (Stokes side) energy positions of the L- and T-acoustic phonons of sapphire.

of their speed of sound, does not significantly overlap with the Gallium spectra. In order to extract quantitative information on the reported excitations, a data analysis has been performed following a memory function approach that has been shown to be well footed on several simple fluids [3, 7]. Within the generalized Langevin equation formalism, it is possible to express the *classical* dynamic structure factor in terms of a complex memory function,  $M(Q, t)$ , related to the interaction details. In particular, in terms of the real and imaginary part of the Fourier-Laplace transform of  $M(Q, t)$ , it holds [3]:

$$S(Q, \omega) = \frac{S(Q)\pi^{-1}\omega_0^2(Q)\tilde{M}'(Q, \omega)}{\left[\omega^2 - \omega_0^2(Q) + \omega\tilde{M}''(Q, \omega)\right]^2 + \left[\omega\tilde{M}'(Q, \omega)\right]^2}.$$

Here the quantity  $\omega_0^2(Q) = KTQ^2/mS(Q)$  is related to the generalized isothermal sound speed through the relation  $c_t(Q) = \omega_0(Q)/Q$ , and can be calculated from the liquid structure once  $S(Q)$  is known. In order to be used as a test function to fit the experimental data, the above expression has to be modified to satisfy the detailed balance condition and must be convoluted with the instrumental resolution function  $R(\omega)$ :

$$I_N^{th}(Q, \omega) = \int \frac{\hbar\omega'/KT}{1 - e^{-\hbar\omega'/KT}} S(Q, \omega') R(\omega - \omega') d\omega'.$$

Taking advantage of the results obtained in several other liquid metals (Li, Al, Na) [7, 12] and fluids (noble gases) [13, 14, 15], we utilized a memory function composed by two relevant time-scales associated to two processes of viscous origin, plus an exponential contribution that accounts for the thermal relaxation process. For the two viscous terms we adopted a simple Debye law (exponential decay) to account for the structural relaxation and an instantaneous approximation (delta-function) for the faster, microscopic contribution. Consequently, the total memory function reads

$$\begin{aligned} M(Q, t) &= (\gamma - 1) \omega_0^2(Q) e^{-D_T Q^2 t} \\ &\quad + \Delta_\alpha^2(Q) e^{-t/\tau_\alpha(Q)} + 2\Gamma_\mu(Q)\delta(t). \end{aligned}$$

Thus the free fitting parameters are  $\tau_\alpha$  (the structural relaxation time),  $\Delta_\alpha(Q)$  (the structural relaxation strength) and  $\Gamma(Q)$  (associate to the microscopic relaxation, and representing the Brillouin line-width in the fully relaxed limit). The value of  $\omega_0(Q)$  has been calculated using the  $S(Q)$  data reported in [9], while the specific heat ratio  $\gamma$  and thermal diffusivity  $D_T$  are deduced by macroscopic data (their  $Q$ -dependence have been neglected). The outcome of the fitting procedure for selected  $Q$ -values, i.e. a comparison between the best fitting line-shape and the experimental spectra, is reported in Fig. 2. Intensities have been normalized using the  $S(Q)$  values of Ref. [9].

In Fig. 3 we report the apparent sound velocity [16] (full dots). At the lower accessible wavevectors, the measured sound velocity ( $\approx 3000$  m/s) still exceed the isothermal value

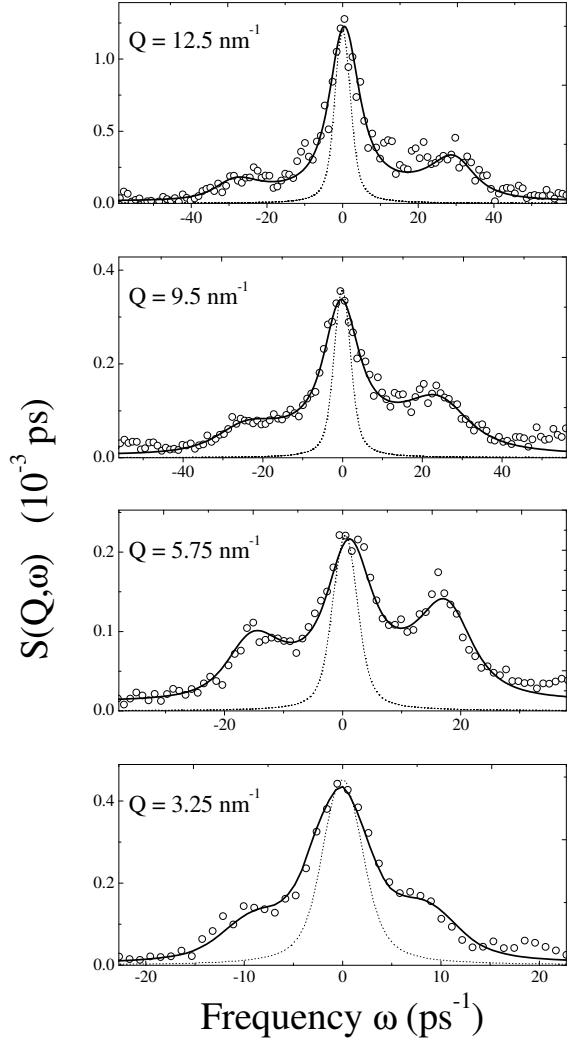


FIG. 2: Selection of IXS spectra ( $\circ$ ) plotted with the fitting function (—) described in the text. The instrument resolution function ( $\delta E \approx 3.0$  meV) is also shown (···).

( $\approx 2800$  m/s) as deduced by ultrasounds measurement [17], a behaviour (the so called positive dispersion of the sound velocity) that is common with many other simple fluids. In the same figure we report the generalized (Q-dependent) isothermal sound velocity ( $\omega_0(Q)/Q$  as deduced by the  $S(Q)$  [9]) (open triangles) that constitutes the low frequency limit of the sound speed, as well as the high frequency limit,  $c_\infty(Q)$  (full line) numerically estimated through the structural data (pair distribution function, interaction potential) [10]. The full triangles come from the best fitted values of  $\omega_0(Q)$  that -in a separate check fitting session- has been left as free parameters. The coincidence of the fitting-derived  $\omega_0(Q)$  values with those derived from the  $S(Q)$  data indicates the robustness of the fitting model. In the inset

the  $Q$ -dependence of the structural relaxation time as derived by the fit is reported. Apart from the very high value found at the lower  $Q$  point, mainly because the width of the central line becomes comparable to the instrument resolution, we find a slightly decreasing value in the range  $0.25 > \tau_\alpha > 0.17$ . It is worth to point out that the relation  $\omega(Q)\tau_\alpha(Q) > 1$  holds in the whole explored  $Q$  range, i.e. the structural relaxation is frozen over the probed timescale. Therefore, the apparent sound speed coincides with the  $c_{\infty\alpha}(Q) = \sqrt{\omega_0^2(Q) + \Delta_\alpha^2}/Q$  (dotted line in Fig. 3). The gap observed at low  $Q$  between the apparent speed of sound and the total  $c_\infty(Q)$  is due to the non-negligible strength of the microscopic process, whose timescale is much shorter than the inverse of the current correlation maxima  $\omega_l(Q)$ , a condition that prevents the system from reaching the fully unrelaxed regime.

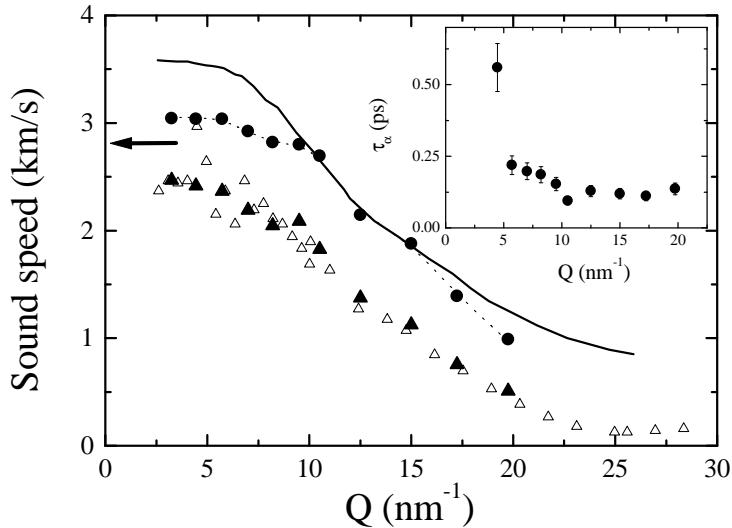


FIG. 3: Speed of sound deduced from the experimental data ( $\bullet$ ), together with the calculated  $c_\infty(Q)$  (—) and  $c_0(Q)$  ( $\triangle$ ) values [9, 10]. The  $c_0(Q)$  determined by the fit ( $\blacktriangle$ ), as far as the  $c_{\infty\alpha}(Q)$  defined in the text ( $\cdots$ ) are also shown. In the inset we report the values of the  $\alpha$ -relaxation time.

A further relevant quantity that can be extracted from the fitting parameters is the generalized ( $Q$ -dependent) longitudinal viscosity  $\eta_L(Q)$ , i.e., in the Langevin equation formalism, the total area of the memory function :  $\eta_L(Q) = \rho(\Delta_\alpha^2\tau_\alpha + \Gamma_\mu(Q))/Q^2$ , reported in Fig. 4. In the upper inset we show the two individual contributions  $\Gamma(Q)$  and  $\Delta_\alpha^2(Q)\tau_\alpha(Q)$ : the viscosity associated with the structural rearrangement turns out to be dominant all over the entire explored  $Q$  range; the contribution coming from the microscopic process (the only one affecting the Brillouin line-width in the present regime) follows -at low  $Q$ - a  $Q^2$  behavior

as already reported in other liquids and glasses [7, 12, 13]. Apart from a low  $Q$  increase, an artifact due to the finite resolution effect and already observed in other systems [7], the total  $\eta_L(Q)$  follows an exponential  $Q$ -dependence, whose origin deserves further investigations. However, the low  $Q$  limit of  $\eta_L(Q)$  can be obtained by extrapolation, and turns out to be in very good agreement with the value  $\eta = 11.4$  cP, determined from the experimental value of the shear viscosity and from the shear-to-bulk viscosity ratio deduced by structural parameters [10]. In the same figure is also reported the  $\eta_L(Q)$  for liquid aluminum at  $T_m$  as obtained from previous experiments [7], which shows a behaviour similar to that of Gallium. To further emphasize the similarity of these different systems, we report in the lower inset a direct spectral comparison at  $Q \approx 9.5 \text{ nm}^{-1}$  (the position of the main peak of the static structure factor is almost the same for Al and Ga). As the absolute temperatures and the instrumental resolutions are different in the two cases, we present the best fitted line-shape according to the model previously discussed. The energy axes has been arbitrary shrunk to wipe out the effect of the different sound speed values. Beside obvious quantitative differences associated -for example- with the different atomic masses and interactions, the two systems at the melting point present very close line-shape. This furtherly confirms the similarity of the high frequency dynamics of liquid Gallium with that of other simple liquids.

In conclusion, we presented an experimental study of the collective high frequency dynamics in liquid gallium at the melting temperature. Evidence for collective acoustic modes has been found in a  $Q$  region extending beyond the hydrodynamic regime up to one half of the structure factor main peak. A generalized hydrodynamic analysis allows a quantitative determination of relevant parameters such as the structural relaxation time and the generalized viscosities. More importantly, it reveals how the main features of the collective dynamics in this system are very similar to the ones reported in different elements such as Li, Na, Al [7] and noble fluids [14, 15]. This is an important indication of how -beside *quantitative* differences- the high frequency dynamics in simple fluids exhibit universal features which go beyond system dependent details such as the electronic structure, bond nature, atomic interaction and structural properties. Since on the observed time-scale the structure of the liquid is frozen ( $\omega_l(Q)\tau_\alpha(Q) \gg 1$ ), one can think of the high frequency dynamics as that of a system with well defined equilibrium position ("glass"). Therefore, the details of the dynamics (microscopic relaxation times, residual viscosity) are fully determined by the

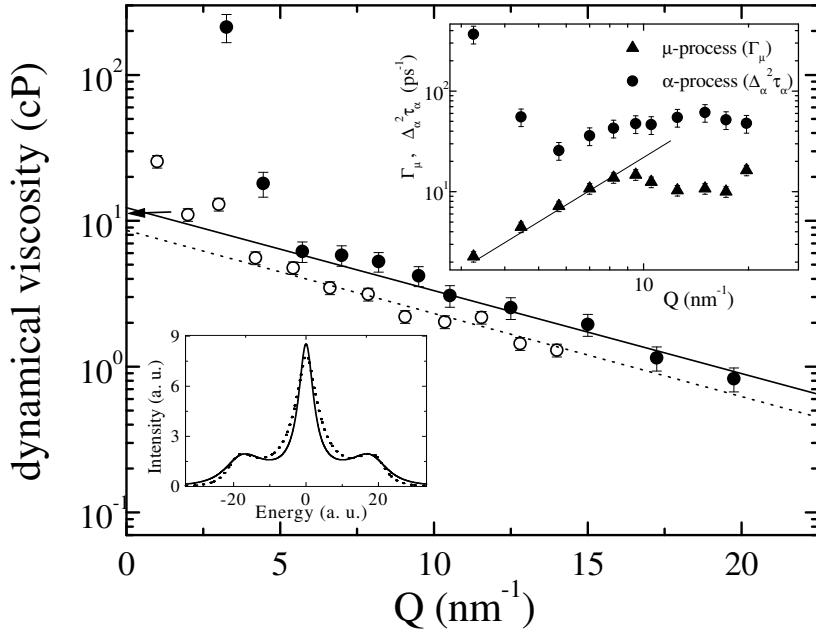


FIG. 4: Values of  $\eta_L(Q)$  as determined by the memory function parameters for Ga (●) and Al (○) [7]. The hydrodynamic value for Ga [10] is also reported (—). Upper inset: partial contributions due to the  $\alpha$ - (●) and  $\mu$ - (▲) process, respectively. The full line emphasizes a noteworthy  $Q^2$  behaviour. Lower inset:  $S(Q, \omega)$  of Ga (—) and Al (···) reported in arbitrary units for comparison.

vibrations of the disordered structure, explaining the observed universality [12, 13]. Finally, although we did not find any evidence for additional modes in the explored  $Q$  range, on the basis of the findings of Ref. [11] we believe that further investigations should be devoted to the higher  $Q$  region.

We are thankful to the ESRF staff for the assistance during the experiment. T.S. gratefully acknowledge M.C. Bellissent Funel for providing  $S(Q)$  data.

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- [16] It is worth to recall that the apparent sound velocity is defined as the ratio of the excitation frequency  $\omega_l(Q)$  to the  $Q$  values. The quantity  $\omega_l(Q)$ , in turn, is the position of the maximum of the longitudinal current correlation spectrum  $J^L(Q, \omega) = \omega^2/Q^2 S(Q, \omega)$ , where  $S(Q, \omega)$  is

obtained by the best fitted parameters, and therefore is resolution deconvoluted.

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